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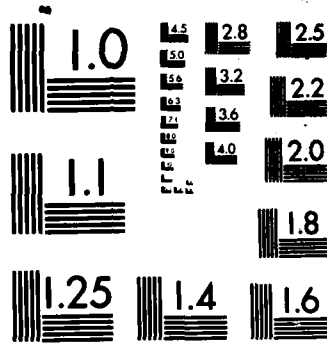
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FINAL REPORT

IMPROVED STRUCTURAL POLYMER ALLOYS AND COMPOSITES

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<p>Substantial progress was made in both experimental and theoretical elements. First, we devised procedures to synthesize (a) sulfonated polysulfone with a controlled and reproducible structure, (b) sulfonated polyaryletheretherketone with <30% sulfonation that has potential as a new high-temperature ionomer, and (c) polyaryletherketone-co-ethersulfone made by a novel ether interchange.</p> <p>Blending studies centered on copolyester LCP's and polybenzimidazole/polyimide combinations. The latter are rendered compatible through specific interaction but which can be phase separated. This finding could result in greatly enhanced opportunities for the use of PBI resins. The major objectives with the LCP blends was to define criteria for miscibility and to improve their processability.</p> <p>Theoretical research was conducted on both LCP/LCP and random coil blends. Particularly important was work on the effect of sequence distribution on phase behavior in random coil blends. A model, containing an ordering parameter, successfully explained the special case of a random/alternating copolymer of the same composition to data.</p>					
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Chief, Technical Information Division

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VII. Abstract

Substantial progress was made in both the experimental and theoretical elements of our program to produce improved polymer alloys and composites. Because our blending program required high temperature copolymers and because these were not available commercially, we had to mount a major synthetic effort. Specifically, we devised procedures to synthesize (a) sulfonated polysulfone (SPSF) - a copolymer with a controlled and reproducible structure, (b) sulfonated polyaryletheretherketone (SPEEK) with <30% sulfonation - a copolymer that has considerable potential as a new high-temperature ionomer, and (c) polyaryletherketone-co-ethersulfone (COPEKS) - a random copolymer made by a novel ether interchange. Definitive papers and patent applications covering these areas are in preparation.

Our blending studies centered on copolyester LCP's (COPEst-LCP) and more recently on polybenzimidazole/polyimide (PBI/PI) homopolymer combinations. The latter represents a broad class of blends rendered compatible through specific interactions but which can be phase separated on the basis of their LCST behavior. This is of major significance and it could result in greatly enhanced opportunities for the use of PBI resins. Potential improvements are foreseen in the price performance profile of PBI, thermal processability for PBI and improved solvent resistance for polyetherimides in miscible blend systems. The synergisms usually associated with phase separated systems remain to be delineated. Broadly based patent applications are in preparation. The major objectives in our work with COPEst-LCP blends has been to define criteria for miscibility in LCP/LCP blends and to prepare blends with improved processability.

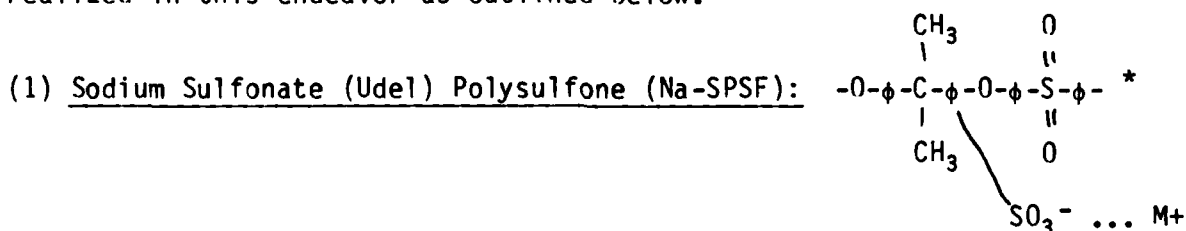
Several of these efforts are currently being scaled-up to prepare larger quantities for engineering property analysis. These include PBI/PI blends based

on commercially available resins, COPEKS and COPEst-LCP's. Also the blending potential of SPEEK is being assessed.

Theoretical research was conducted on both LCP/LCP and random coil blends. Particularly important was modeling work on the effect of sequence distribution on phase behavior in random coil blends. A model was developed, containing an ordering parameter, and successfully compared to the special case of a random/alternating copolymer of the same composition - in this case poly(vinyl chloride)/ chlorinated polyethylene (PVC/CPE). Our next effort will be devoted to extending some of these concepts to block copolymers.



VIII. Materials Research Accomplishments

Our goal has been to prepare new generations of high performance polymer alloys and blends, with a target temperature range of 300 to 400°C. As has been previously stressed, the opportunities for forming useful blending pairs is greatly enhanced when at least one of the blending pairs is a copolymer. Further enhancement occurs when both components are copolymers. This principle has placed considerable emphasis on the synthesis of new high-temperature copolymers since these are not available commercially. Some success has been realized in this endeavor as outlined below.

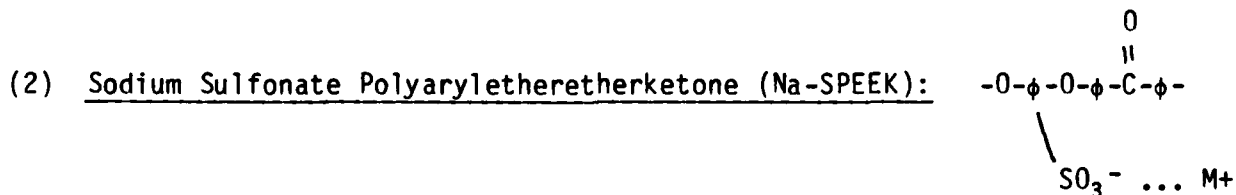


We have developed improved synthesis procedures to produce Na-SPSF copolymers with well-defined, random, homogeneous structures for sulfonation levels <30%. Previous methods described in the literature produce ill-defined heterogeneous copolymers. Na-SPSF copolymers are not as thermally stable as we require for use as high-performance ionomers, but they are more soluble and tractable than the sulfonated PEEK to be described subsequently. Thus, they should be especially useful in model studies of solution behavior and membrane performance.

We are preparing a pair of definitive papers for publication. These will describe the synthesis procedures, a comprehensive thermal analysis (DSC, TGA

*The symbol $\text{-}\phi\text{-}$ is used to represent the phenyl ring with a para () linkage. $\text{-}\phi_m\text{-}$ will be used to represent a meta () linkage.

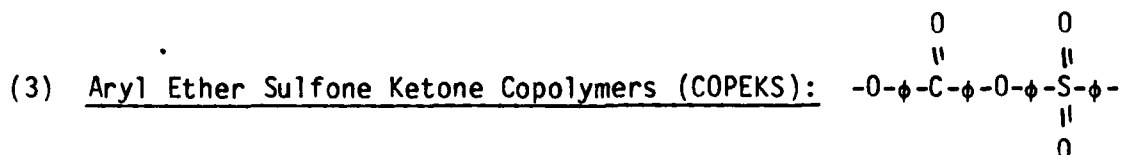
and DMA), molecular structure vs cluster formation and blends of Na-SPSF of differing composition. Pairs of the latter type are part of a new class of ionomeric alloys known as Ionomeric Interpenetrating Polymer Networks (IIPN). A patent application is in preparation for the synthesis procedure.



Earlier published methods for preparing SPEEK produced ill-defined, heterogeneous copolymers, with sulfonation levels generally greater than 20 to 30%. The latter are higher than one normally employs in membrane and ionomer applications. We have developed two synthesis procedures to produce random, homogeneous copolymers over the entire accessible composition range of zero to 100% sulfonation. One method is applicable to the lower sulfonation levels (0 to 40%) and thereby allows the production of an entirely new series of ionomers. Indeed, we believe that the ionomers produced by this method are the most solvent and heat resistant ionomers yet produced. The other method is applicable to higher sulfonation levels (30 to 100%), and it represents an improved version of earlier methods. A patent application has been drafted to cover the first method.

Sodium SPEEK copolymers appear to be sufficiently stable, both thermally and chemically, to merit consideration as high performance ionomers, IIPN's and membranes - perhaps to temperatures as high as 300 or 400°C. Sodium SPEEK copolymers, covering the 5 to 100% sulfonation range, have been extensively examined by DSC, TGA, SAXS and moisture absorption techniques to elucidate their struc-

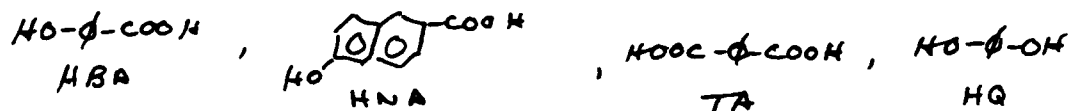
ture, both in terms of ionomeric cluster domains and crystallinity. A comprehensive paper is in preparation to describe the latter results. Blending studies have been initiated, and preliminary results will be published as a note. Studies to further define the SPEEK polymer structure continue.



Attempts to prepare these copolymers directly from the monomers results in "blocky", heterogeneous structures because of the wide differences in the reactivity of the monomer pairs. A general class of random, homogeneous copolymers of this type can be synthesized via a novel ether interchange procedure we have developed. COPEKS might be useful as engineering materials in their own right and as blending agents for the parent homopolymers: polyether sulfone (PES) and PEK. Blends with PES might improve the poor environmental stress crack resistance (ESCR) usually associated with this otherwise high performing resin, and blends with PEK might be useful in modulating its crystallinity or in improving its processability. The laboratory synthesis procedure is being scaled-up to permit study of these possibilities. Materials prepared in the laboratory have been characterized by the usual thermal methods (DSC, DMA and TGA) and GPC analysis is underway. A paper for publication and a patent application are anticipated shortly. Studies of blends of COPEKS with other types of homopolymers and copolymers are being planned.

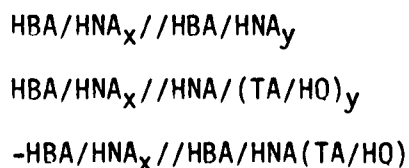
In addition to these major developments in the synthetic area, a number of important accomplishments have been realized in our blending work.

(4) Copolyester Liquid Crystal Blends (CoPEs+-LCP):



As has been widely publicized, thermotropically processable LCP's based on copolyester chemistry are in the process of being commercialized by Dartco and Celanese. These are high performance resins in every sense of the word, somewhat equivalent to PEEK (produced by ICI) in performance. The first polyester LCP, based on hydroxy benzoic acid (HBA) alone, was not fusible and therefore not melt processible; techniques derived from powder metallurgy - sintering - had to be employed. LCP's based on copolyester chemistry are fusible (albeit at high temperatures) and thereby partly overcome this fabrication problem. In an attempt to gain additional improvements on this situation, we are investigating the rheology of blends of copolyesters based on the monomers shown above. Other equally important objectives are to establish miscibility criteria for LCP blends and to use these observations to expand the scope of the Karasz-MacKnight theory to liquid crystal copolymer (LCCoP) blends.

The rheological studies were performed in the Haake-Buchler mixer, and the results are expressed both in terms of the torque and power law index. Solid state properties were defined primarily by DSC and DMA. The copolymers and blends of interest are listed below:



The rheological behavior observed to date for LCP/LCP blends can be divided into two types. In the first type the torque and power law indices obey

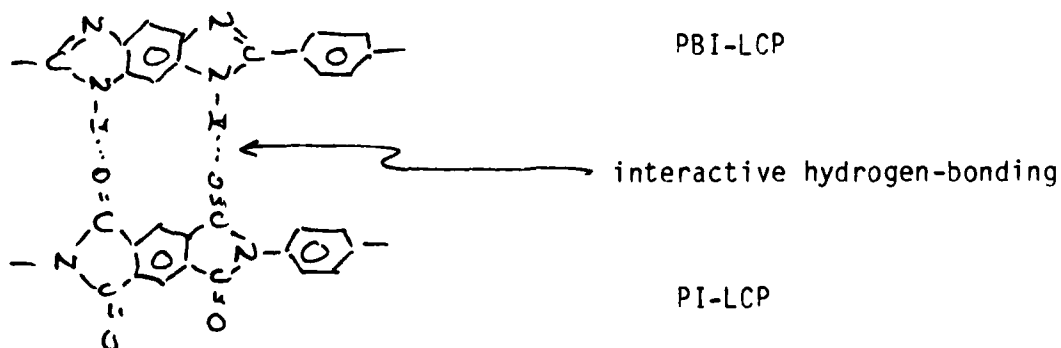
a simple rule of mixtures. In the second type, a minimum in the torque and a corresponding maximum in the power law index are observed with a variation in composition. These results are currently being interpreted in terms of the system's melt miscibility (first type) or immiscibility (second type). DSC scans were run on samples of each type directly as they were received from the mixing equipment. Blends displaying rule-of-mixture rheological behavior displayed a minimum in the melting temperatures which is typical of a miscible mixed crystal system. The effect of annealing is under investigation. Blends of the second type displayed a more complex scan profile which has not yet been interpreted.

DMA have been performed on samples prepared by compression molding. The base copolymers display two transitions within the range of 0 to 200°C. As with the rheological behavior, two types of behavior are observed, one indicative of miscible behavior, the other of immiscible behavior.

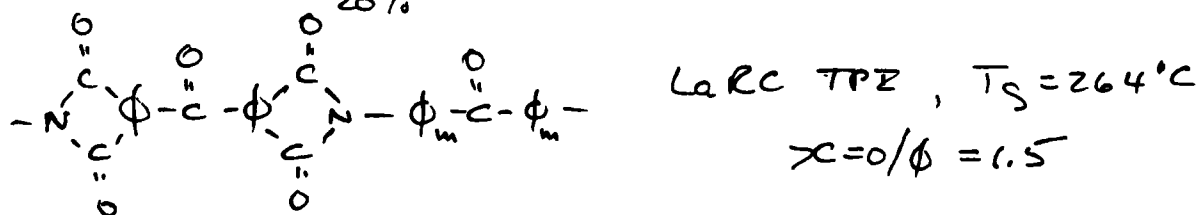
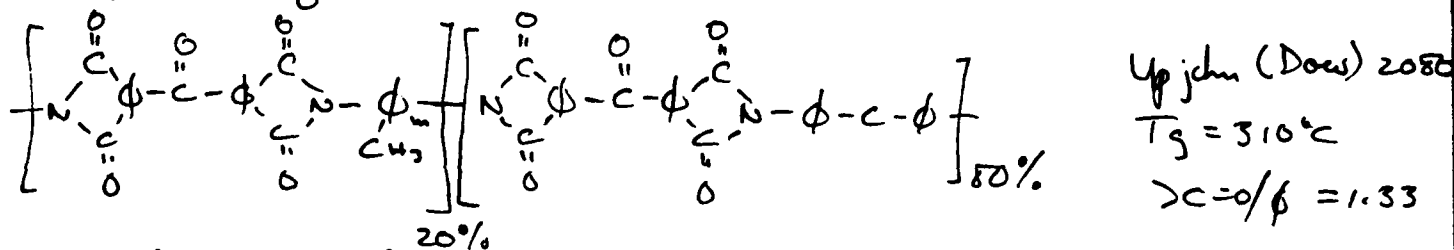
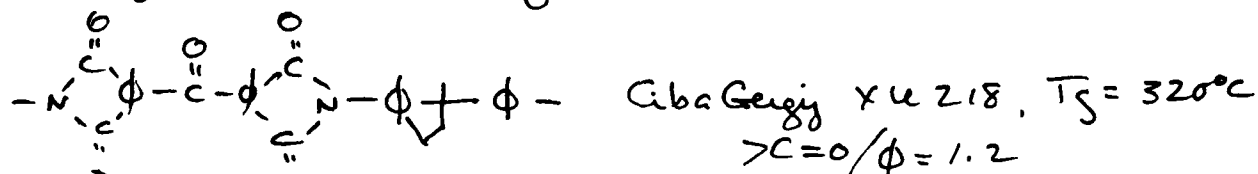
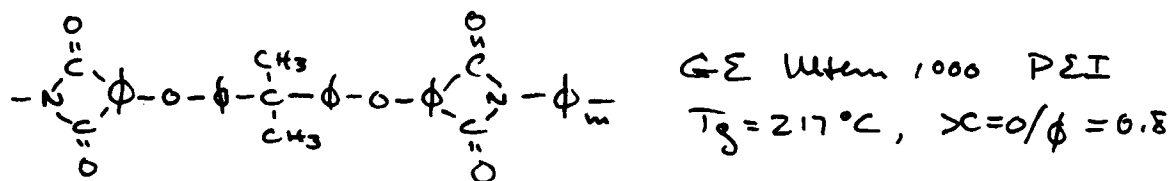
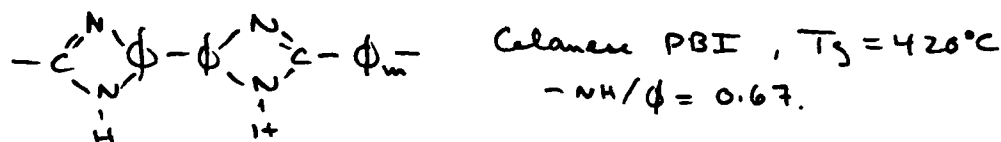
Efforts are targeted toward drafting a paper for publication in the near future. Plans for scale-up will be delineated subsequently.

(5) Polybenzimidazole/Polyimide Blends (PBI/PI):

We have discovered a broad class of compatible homopolymer pairs, formed through interactive hydrogen bonding. As conceptually illustrated below for LCP pairs, the PBI supplies the -NH group while PI supplies the >C=O group.



To date we have established the validity of the concept illustrated above using the commercially available amorphous polymers listed below. Listed are T_g and the ratio of either the -NH groups or the $>C=O$ groups per phenyl ring (ϕ) in the repeat unit. An essential part of the concept is to control the degree of compatibility through variation of the $>C=O$ group/ ϕ group ratio compared to the -NH group/ ϕ group ratio which is fixed at 0.67 for the Celanese PBI we are currently working with. For the PI's listed $>C=O/\phi$ ranges from 0.8 to 1.5.



The polyetherimide (PEI) Ultem 1000 (GE) displays the weakest compatibility ($\chi C=0/\phi=0.8$). Single phase film samples can be prepared by solvent casting if moisture is rigorously excluded and if the blend temperature is always maintained at $T < T_g$. If moisture is present during the early stages of film formation and if $T > T_g$, phase separation will result. In homogeneous situations, we expect to derive rule of mixture mechanical properties with PEI serving as a plasticizer for PBI and with a performance profile analogous to the polystyrene/polyphenylene oxide situation. Early results suggest that enhanced solvent resistance of PEI to chlorinated solvents is obtained. Property advantages in phase separated PBI/PEI pairs remain to be investigated.

The other three PI/PBI pairs listed above are miscible above T_g so that these might be thermally processable. This is an important point because PBI, with its high T_g (420°C), cannot be thermally processed. The three PI's in question have $\chi C=0/\phi$ ranging from 1.2 to 1.5. Conceptually, the LaRC TPI would seem to offer the best chances of success because, of the three, it is the most thermally stable and has the lowest T_g .

We are currently working with CRC to prepare samples of sufficient variety and quantity to fully exploit the promise of our early work. PBI/PEI pairs will be solvent processed into films and fibers. The other three PBI/PI pairs will be thermally processed, either in compression molding or extrusion operations, into three dimensional parts.

Patent applications are in preparation to obtain the broadest possible coverage.

IX. Theoretical Research Accomplishments

LCP Blends

A model for describing blends was utilized to make predictions about the expected miscibility for various semiflexible systems. The first system consisted of a random coil polymer of some fixed contour length with a second component of varying length and flexibility. The first calculation assumed athermal mixing conditions. When the second component was assumed to be a rigid rod, the random coil component remained in the isotropic phase while the rigid rod component remained in the anisotropic phase, almost exclusively. As the flexibility of the second component was increased, the random coil still was excluded from the anisotropic phase but the semiflexible molecule could be made to enter the isotropic phase.

Further work incorporated the effects of different lengths of the two components as well as the effect of addition of a heat of mixing term. Increasing the lengths of the components seemed to favor phase separation even under athermal mixing conditions. Addition of a heat of mixing term to the calculations did not affect the exclusion of the random coil from the anisotropic phase, an effect which seemed to be entropy controlled. However, addition of a negative heat of mixing did increase the possibility of finding the semiflexible component in the isotropic phase. Similarly, a positive heat of mixing decreased the likelihood of the semiflexible component entering the isotropic phase.

Random Coil Blends

Theoretical studies were conducted on the effect of sequence distribution on phase behavior. In general, theories describing the phase behavior of copolymer blends have assumed a random distribution of monomer units in the copo-

lymer. We have introduced a parameter, θ , which describes the binary sequence distribution of the monomers in a copolymer chain. By varying θ , a block, random or alternating copolymer can be described. It was assumed that the interaction energy between a monomer of homopolymer C and the monomer A (or B) in the copolymer AB was mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. It was found that the sequence distribution significantly affects the degree of compatibility between the polymers AB and C. For a fixed composition, there was an optimal range of θ values (or sequence distributions) for which the C/AB system was miscible.

A special case of the foregoing was a blend where both copolymers have the same composition but differ only in sequence distribution: for example, a blend of 50:50 alternating copolymer with a 50:50 random copolymer. The general formula was adapted to this case, with which we can theoretically confirm the experimental observation that PVC and chlorinated polyethylene (CPE) of the same composition are immiscible. From experimental data on PVC/CPE mixtures, we evaluated the χ parameters required by our theory and consequently calculated $\chi_{CH_2:CHCl}$.

In another study, a theoretical model was devised to incorporate the effects of specific interactions and compressibility on phase behavior. In the first case, interaction occurs only if the mers have the same orientation or they are in the same energy state. The effects of compressibility were incorporated via an appropriate partition function. The influence of these effects on phase behavior was described graphically.

X. Publications

1. "Effect of Sequence Distribution on the Miscibility of Polymer/Copolymer Blends", A.C. Balazs, I.C. Sanchez, I.R. Epstein, F.E. Karasz, W.J. MacKnight, in press, Macromolecules.
2. "Copolymer/Copolymer Blends: Effect of Sequence Distribution on Miscibility", A.C. Balazs, F.E. Karasz, W.J. MacKnight, H. Ueda, I.C. Sanchez, submitted to Macromolecules.
3. "The Effect of Sequence Distribution in Block Copolymers", A.C. Balazs, F.E. Karasz, W.J. MacKnight, in preparation.
4. "The Effects of Specific Interactions & Compressability on Polymeric Phase Behavior", A.C. Balazs and I.C. Sanchez, in preparation.
5. "The Sodium Salts of Sulfonated Polyaryletheretherketone (PEEK): Preparation & Characterization", C. Bailly, D.J. Williams, F.E. Karasz and W.J. MacKnight, in preparation.
6. "DSC Studies of Blends Based on Sulfonated PEEK", C. Bailly, D.J. Williams, W.J. MacKnight, F.E. Karasz, in preparation.
7. "Synthesis of Sulfonated Udel Polysulfone", J.F. O'Gara, D.J. Williams, F.E. Karasz and W.J. MacKnight, in preparation.
8. "Studies of Blends Based on Sulfonated Polysulfones", J.F. O'Gara, D.J. Williams, W.J. MacKnight, F.E. Karasz, in preparation.
9. "Polyacryletherketone-co-ethersulfone by a Novel Ether Interchange Reaction", J.L. Cercena, D.J. Williams, F.E. Karasz, W.J. MacKnight, in preparation.
10. "Model System for Liquid Crystal Containing Polymer Blends", M.T. DeMeuse, M. Jaffe, F.E. Karasz and W.J. MacKnight, in preparation.

XI. Patent Applications in Preparation

1. "Preparation of Novel Sulfonated PEEK Copolymers", C. Bailly, D.J. Williams, F.E. Karasz, and W.J. MacKnight.
2. "Methods of Preparing Improved Structures of Sulfonated Polysulfone", J.F. O'Gara, D.J. Williams, F.E. Karasz and W.J. MacKnight.
3. "On the Synthesis of Polyaryletherketone-co-ethersulfones", J.L. Cercena, D.J. Williams, F.E. Karasz and W.J. MacKnight.
4. "Blends of Polybenzimidazoles and Polyimides", D.J. Williams, L. Leung, F.E. Karasz and W.J. MacKnight.
5. "Blends of Polybenzimidazoles and Polyetherimides," L. Leung, D.J. Williams, F.E. Karasz and W.J. MacKnight.
6. "Blends of Polybenzimidazoles and Polyimides, Wherein one is a Liquid Crystal Polymer", D.J. Williams, F.E. Karasz and W.J. MacKnight.
7. "Polybenzimidazole-Polyimide Sintering Systems", D.J. Williams, F.E. Karasz and W.J. MacKnight.

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